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Polymeric coatings for photostability enhancement of poly(p-phenylene vinylene) derivative films

Polymeric coatings for photostability enhancement of poly(p-phenylene vinylene) derivative films

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Abstract

Poly(p-phenylene vinylene) (PPV) derivatives are an important class of conjugated polymers, known for their applications as electroluminescent materials for light-emitting devices and sensors. These derivatives are highly susceptible to photodegradation by the combined action of oxygen and light. Here, the use of various commercial polymers as protective coatings against the photodegradation of PPV derivatives was explored. Cast films of two similar PPV derivatives, poly[(2-methoxy-5-n-hexyloxy)-p-phenylene vinylene] and poly[2-methoxy-5-(2-ethylhexyloxy)-p-phenylene vinylene], were submitted to photodegradation by exposure to white light under atmospheric conditions in order to verify if the type of side chain (linear or branched) had an effect on the photodegradation. No significant differences in the photodegradation behaviour between the two polymers were noticed. The following commercial polymers were tested as protective coatings for the PPV derivative cast films: 99 and 80% hydrolysed poly(vinyl alcohol) (PVA) and starch. The best results were achieved using coatings of 99% hydrolysed PVA, which increased about 700 times the time necessary for complete degradation of the PPV derivative films. The results show the effectiveness of this coating in minimizing and, possibly, controlling the effects of the photodegradation of PPV derivative films, which can be useful in many applications, e.g. oxygen sensors.
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Keywords: PPV derivative; photodegradation; coatings; conjugated polymers

INTRODUCTION

Poly(p-phenylene vinylene) (PPV) derivatives are an important class of conjugated polymers, known mainly for their applications as electroluminescent materials for light-emitting devices and sensors.[1] Compared to small organic molecules, PPV derivatives are easily processed, more stable and are good candidate materials for flexible devices. However, PPV derivatives are highly susceptible to photo-oxidation[2–17] and expensive; and time-consuming methods of encapsulation are required in order to minimize their photodegradation. The main cause of photodegradation in these conjugated polymers is the combined action of oxygen and light that leads to cleavage of the vinyl double bonds in the polymer backbone,[5] with the introduction of oxygen atoms as carbonyl groups, thus decreasing the conjugation length. Earlier studies have shown that the degradation only occurs in the simultaneous presence of oxygen and light, since films of PPV derivatives stored in the dark or exposed to light in vacuum did not show significant photodegradation.

The rate of photodegradation depends on the film thickness, the power and wavelength of the incident light as well as the method used to prepare the films.[17] Thicker films degrade more slowly than thinner ones, probably due to differences in oxygen permeation throughout the films and also due to the decay in the light transmission through the films, as stated by Beer's law. Light of all wavelengths (UV and the whole of the visible range) degrades PPV derivatives and the rates of degradation are higher for shorter wavelengths. Films of PPV derivatives prepared using the Langmuir–Blodgett technique tend to degrade more slowly than films using the casting method probably due to differences in the morphology induced by the film-forming technique (Langmuir–Blodgett films tend to be denser).[17]

In order to minimize the photodegradation of PPV derivatives, several approaches have been attempted, such as: changing the molecular architecture of the derivatives to include electron-withdrawing groups in the polymer backbone, therefore decreasing the rate of oxidation; the use of blends with commercial polymers; and the use of coatings as protective layers or encapsulations[18–22] in order to minimize the exposure to atmospheric oxygen. Luminescent devices are generally fabricated by coating glass (or other substrate) with a thin film of the luminescent polymer deposited by solution processing. It is desirable that the coating be applied onto the luminescent layer around room temperature in order to avoid temperature effects on the luminescent film surface. Also, the coating solvent must not dissolve the luminescent layer. Generally epoxy, polyurethane and vinylic polymers which have low oxygen permeability can damage the luminescent layer by partial dissolution (if applied by solution) or by the high temperature of application (if applied by melting). Polymers containing hydroxyl groups, where strong hydrogen bonds are present, usually present low oxygen permeability and

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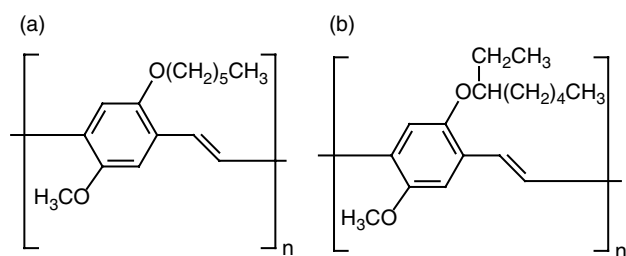b Universidade Federal de São Carlos, UFSCar, CP 3031, 18043-970, Sorocaba, SP, Brazil

(a)

(b)

Figure 1. Chemical structures of the luminescent polymers: (a) OC_1OC_6-PPV; (b) MEH-PPV.

are soluble in water or low-molecular-weight alcohols, which are non-solvents for the PPV derivatives. Also, they are usually transparent in the visible region which is essential for applications in optical sensors. Therefore water-soluble hydroxylated polymers that possess good film-forming capabilities are good candidates as protecting layers against oxidation of PPV derivative films, since they can be coated on the PPV derivative layer without damaging the film surface. Here, we report on a preliminary evaluation of some protective layers made of commercial hydroxylated polymers with the aim of reducing photodegradation effects on PPV derivative films, without interfering with their main optical properties. The control of the photodegradation process can be very useful in designing sensors, as, for example, in sensors for oxygen exposure.

EXPERIMENTAL

Poly[(2-methoxy-5-n-hexyloxy)-1,4-phenylene vinylene] (OC_1OC_6-PPV) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) were synthesized according to procedures similar to those reported by Wudl and Srdanov.[23] The chemical structures are shown in Fig. 1. Luminescent cast films were obtained by casting chloroform solutions (generally 0.3 mg mL^{-1}, and 0.1 mg mL^{-1} only for the films used in kinetics measurements) of the PPV derivatives onto B270 glass slides in the dark. Only films with similar absorbance values (similar thicknesses) were used in the comparisons. Films were coated by dipping the substrates, with the PPV derivative films, in 2 wt% solutions of commercial polymers in ethanol/water (1 : 1), and drying under reduced pressure at 40 °C for at least 2 h. The coating polymers used were 80 and 99% hydrolysed poly(vinyl alcohol) (PVA, sometimes also referred to as PVOH or PVAl; Aldrich) and regular corn starch Amidex (28 mol% amylose; Corn Products). All coatings formed films of good optical quality and which were completely transparent in the visible region. The coating thicknesses were around 1 µm in all cases.

Photodegradation experiments were performed by illuminating the films with white light from a halogen lamp (50 W, 12 V; Osram), placed at a fixed distance (about 30 cm) from the sample, yielding 17 mW cm^{-2} of power at the sample surface. UV-visible spectra were recorded with a Hitachi U2001 spectrophotometer in transmission mode. The illumination was performed in ambient atmosphere in open air at a controlled temperature of 25 °C, with the polymer films facing the lamp. The illumination was also performed inside a Shimadzu RP5301 spectrofluorimeter, keeping the samples exposed to an exciting beam at 490 nm (ca 3 mW cm^{-2}), and recording the photoluminescence (PL) spectra at time intervals of ca 100 s.

RESULTS AND DISCUSSION

The polymers used in the protective coatings should not dissolve the luminescent polymers and must show good adhesion to the luminescent films. Among the several polymers tested, only the hydroxylated PVA and starch show acceptable adhesion properties to the luminescent films and are soluble in solvents that do not dissolve the luminescent films. The value of the permeability coefficient for unmodified starch[24] is ca 1.0 cm^3 O_2 m^{-2} day^{-1} atm^{-1}. PVA is prepared by the partial hydrolysis of poly(vinyl acetate), thus being a copolymer of vinyl alcohol and vinyl acetate. The value of the permeability coefficient for 99% hydrolysed PVA (copolymer containing only 1 mol% of vinyl acetate), under ambient conditions, is[25] ca 0.06 cm^3 O_2 m^{-2} day^{-1} atm^{-1}, thus being ca 15 times less permeable to oxygen than starch.

The mechanism of the photodegradation process of PPV derivatives is extensively described in the literature[2–17] and thus it will not be discussed in detail here. The main feature in this process, which requires illumination in the presence of oxygen, is the cleavage of the double bond of the vinylene group and the introduction of oxygen forming a carbonyl group, decreasing the conjugation length and hence the wavelength of the maximum absorption (λ_{max}) of the polymer. The photodegradation of cast films of OC_1OC_6-PPV on glass, neat and coated with starch or PVA, was followed by absorption in the visible region (Fig. 2). All films were exposed continuously to the white light under ambient conditions for almost 120 h and visible spectra recorded after several periods of illumination. For clarity, some spectra are not shown in the figure. All coated films show a decay in the absorbance due to the photodegradation process. However, the results obtained with the 99% hydrolysed PVA-coated film show a very small decay compared to the starch-coated film. Although OC_1OC_6-PPV and MEH-PPV have differences in solubility and film-forming capabilities, both show very similar results in all photodegradation experiments carried out. Therefore, in this case, differences in the side chain (branched and linear) do not affect the photodegradation process and all results shown here are valid for both PPV derivatives tested. It is worth noting that, under the conditions used, films of all polymers used as coatings in this work showed no signs of degradation upon illumination, as evident from their Fourier transform infrared spectra.

Figure 3 shows the absorbance decay of OC_1OC_6-PPV films, neat and coated, at the wavelength of maximum absorbance (490 nm) of the pristine film, upon exposure to light. The values are normalized by the initial absorbance (A_0) of the films. Only the film coated with PVA shows a degradation behaviour different from that of the neat luminescent film. The starch coating is not effective in minimizing the photodegradation effects, presenting an absorbance decay similar to that of the neat film. The absorbance of the neat and starch-coated films decrease to about 50% of the initial absorbance after 4000 min of illumination (ca 67 h), while the PVA-coated film shows only a 5% decrease of the initial absorbance after the same exposure time.

The photodegradation of the PPV derivative films usually follows first-order kinetics[26] and can have one or more stages, since it seems to occur first at the illuminated surface and then in the bulk of the film.[27,28] In order to estimate the enhancement in the photostability of the PPV derivative films with the use of the PVA coatings, a semi-logarithmic plot of the absorbance decay as function of illumination time was constructed and the degradation rates estimated by the calculation of the angular coefficients obtained by linear fitting. Films of both PPV
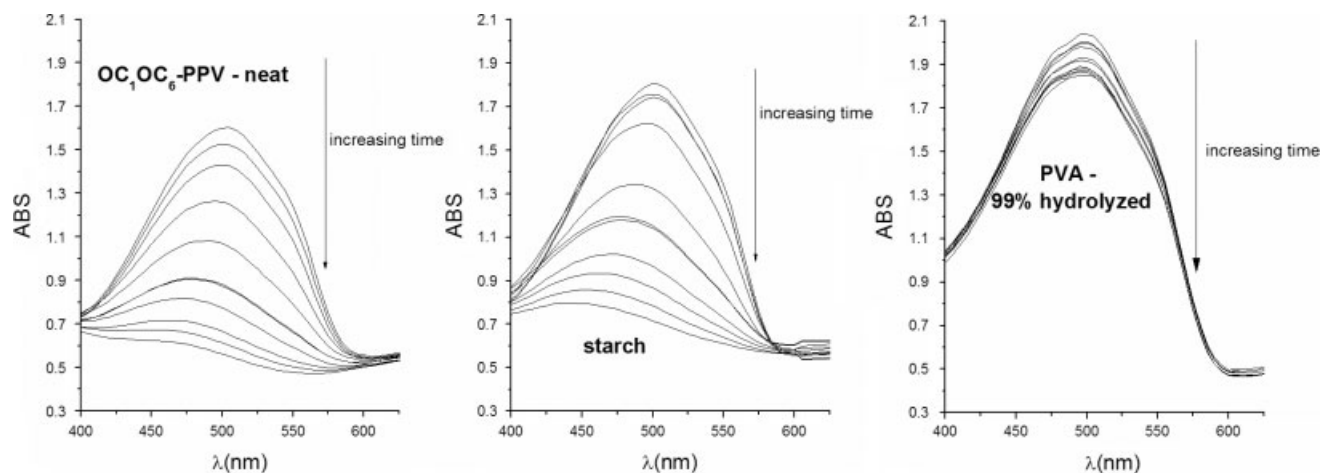
Figure 2. Absorbance decay of OC_1OC_6-PPV films, neat and coated with various polymers, for a light exposure period of 7100 min (about 118 h).
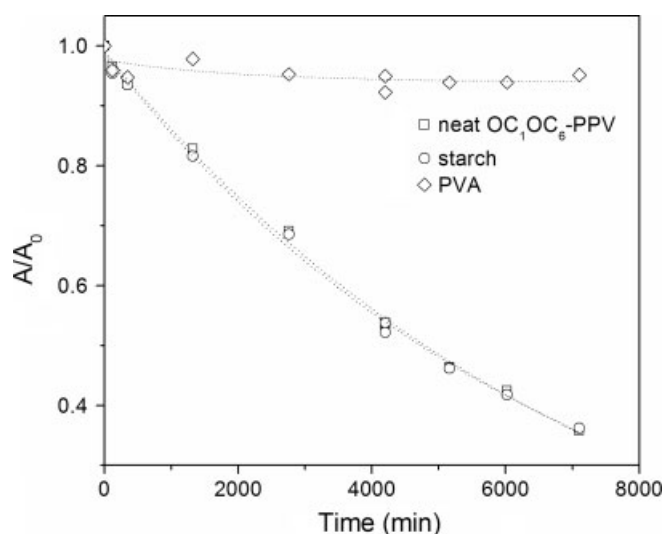

Figure 3. Normalized absorbance decay at 490 nm of OC_1OC_6-PPV films cast on glass, neat and coated with the two polymers.

derivatives show a dependence of the degradation rate upon film thickness: thinner films (ca 5–10 nm) show a mono-exponential photodegradation behaviour and thicker films a bi-exponential one. Since both derivatives show similar behaviour, only MEH-PPV was used for this experiment. Thin films of MEH-PPV with similar thicknesses (ca 30 nm) were used in order to reduce the experiment time to follow the absorbance of the samples until complete degradation. In order to determine if the degree of hydrolysis affects the performance of the PVA coating for protecting the PPV film from photodegradation, two samples coated with 99 and 80% hydrolysed PVA were used. The absorbance values were normalized and corrected for the absorption at infinite time (A_{00}) – the time corresponding to complete discoloration of the samples. The films, in all cases, after complete discoloration maintain their form and optical quality, showing no signs of cracking or cloudiness. In the case of the samples coated with 99% hydrolysed PVA, after 35 days of continuous illumination, the samples were not completely degraded and the value of A_{00} was taken as being equal to the glass substrate absorbance at 490 nm (0.055). Figure 4(b) shows the absorbance decay for samples of

MEH-PPV coated with 80% hydrolysed PVA and Fig. 4(c) that for samples coated with 99% hydrolysed PVA. For illustration, the absorbance decay for a neat film is shown in Fig. 4(a). The absorbance decay for 80% hydrolysed PVA shows a behaviour similar to that of the MEH-PPV neat film. However, the time necessary to completely degrade the film protected with 80% hydrolysed PVA was substantially longer compared to the neat film. Neither decays can be fitted by a single line, but can be divided into two stages (bi-exponential behaviour). The reason for this bi-exponential behaviour is not yet completely clear, but could be related to the change of the photodegradation profile from the surface of the film to the bulk.[27]

The films coated with 99% hydrolysed PVA show mono-exponential absorbance decay. Moreover, after 35 days of continual exposure to the light, the films coated with 99% hydrolysed PVA are not completely degraded: the films are still orange, showing 70% of the initial absorbance value at 490 nm.

The values of the slopes (k) of the plots shown in Fig. 4, for the neat sample and those coated with both PVAs, are listed in Table 1. For the bi-exponential curves, the slope for the initial times (first stage) is designated as k_a and for the second stage as k_b. Only the values obtained for samples of similar thickness (or similar initial absorbance values if absorptivity is similar) can be compared, since there is a dependence of the absorbance decay rates on the thickness of the samples.[17] Therefore these values are only valid for samples with thicknesses of ca 30 nm. The greater the thickness, the lower is the absorbance decay for the same period of illumination. This thickness dependence is due to the decrease of the light transmission across the film, being exponential as described by the Beer–Lambert law, and to the oxygen concentration throughout the film, which depends on the oxygen permeability of the coating and the diffusion of oxygen through the luminescent film.[28] As our samples used for the rate calculations have similar thicknesses and the coatings are transparent in the visible region, the decrease of the light transmission will be similar in all samples as will be the diffusion of oxygen. Thus, the results obtained here can be due only to differences in the oxygen permeability of the coatings. The value of the coefficient of oxygen permeability for 99% hydrolysed PVA under ambient conditions is very low, ca 0.06 cm^3 O$_2$ m^{-2} day^{-1} atm^{-1}.[24] This value depends on the degree of hydrolysis of the polymer. The oxygen permeability increases with the content of vinyl acetate in the copolymer and
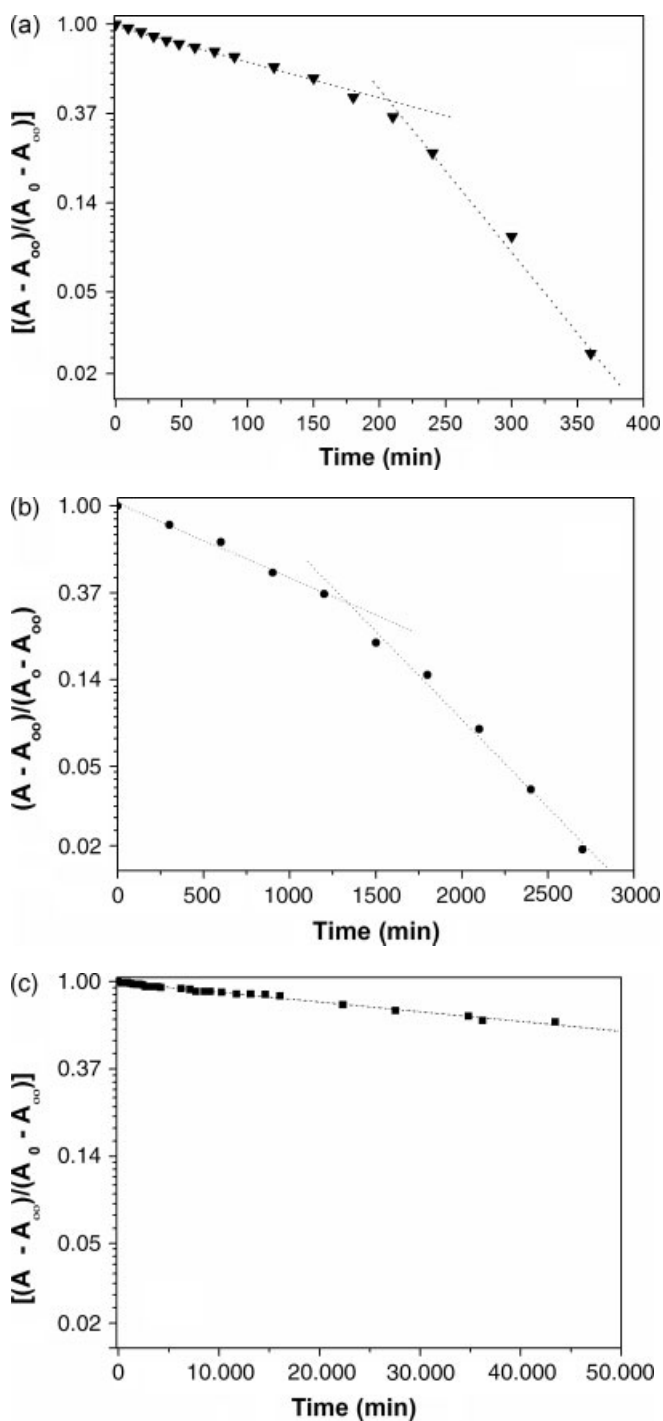
Figure 5. PL spectra of the neat MEH-PPV film on glass compared to the coated films.

Figure 4. Normalized absorbance decay at 490 nm of MEH-PPV films: (a) no coating; (b) coated with 80% hydrolysed PVA; (c) coated with 99% hydrolysed PVA.

pure poly(vinyl acetate) has a coefficient of oxygen permeability of *ca* 3.5 cm^3 O$_2$ m^{-2} day^{-1} atm^{-1}.[25] The value is also affected by the relative humidity, but the 99% hydrolysed PVA is much less affected than the 80% hydrolysed PVA.[29]

For the first stage of the photodegradation, the rate for the samples coated with 80% hydrolysed PVA is about four times lower than that for neat MEH-PPV. For the second stage, comparing the rates for the 80% hydrolysed PVA-coated films with neat film, there
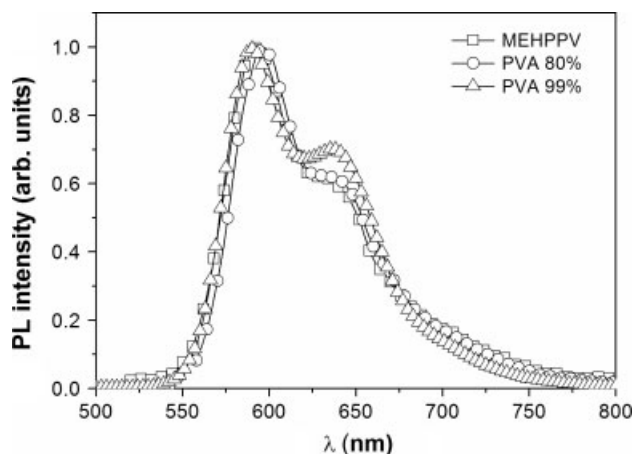
is a decrease of the rate by one order of magnitude. This result indicates that the 80% hydrolysed PVA coating is rather efficient in retarding the photodegradation process. For the films coated with 99% hydrolysed PVA, just one stage is evident from the absorbance decay values, and the rates calculated are significantly lower than the values obtained for both stages of the neat luminescent film. This result shows that the hydroxyl content in the PVA coating plays an important role in the protecting process.

Table 1 also gives the total degradation time, which is the time necessary for the absorbance of the film to reach the glass absorbance (0.055) at 490 nm. The values of total degradation times are only valid for samples with similar thicknesses, as the used here (*ca* 30 nm), since the degradation rates have a thickness dependence.[17] In the case of the 99% hydrolysed PVA, this time was estimated by extrapolation of the linear fitting obtained for the absorbance decays for the value close to the glass absorbance (0.055). The 80% hydrolysed PVA coating increases the total degradation time by about 8 times. For the 99% hydrolysed PVA coating, the increase in the predicted degradation times is much higher, *ca* 700 times.

It is important to note that the coatings do not affect significantly the shape and the wavelength of maximum emission of the PPV derivatives, as can be seen in Fig. 5 showing the PL spectra of MEH-PPV films. The spectra resemble those of MEH-PPV published previously.[30,31] The emission properties are much more sensitive to photodegradation than the light absorption, and thus the PL spectra of two films (OC$_1$OC$_6$-PPV), one neat and the other coated with 99% hydrolysed PVA were recorded upon light exposure. The degradation experiment was carried out by placing the cast films on glass inside the spectrofluorimeter, continuously exposing them to the 490 nm excitation beam and recording the PL spectra. The experiment was carried out for 90 min. The intensity of the PL signal at 595 nm (maximum emission wavelength for non-degraded OC$_1$OC$_6$-PPV) was plotted against the time of exposure. The results are shown in Fig. 6. Also in this case, 99% hydrolysed PVA shows a positive effect on minimizing the photodegradation of the PPV derivative and no signs of degradation are observed in the exposure period used. It is worth noting that, for the neat films, even the low exposure times required for recording a few consecutive spectra degrade the material leading to different PL intensities.

Table 1. Slopes of the absorbance decay plots and total degradation times for neat and coated MEH-PPV films

Sample	k_a ($\times 10^{-4}$ min^{-1})	k_b ($\times 10^{-4}$ min^{-1})	Total degradation time (h)
Neat MEH-PPV	39	134	7.5
Coated with 80% hydrolysed PVA	9	20	64
Coated with 99% hydrolysed PVA	0.1	–	5760[a]

[a] Estimated by extrapolation of absorbance at 490 nm to the value of 0.055.
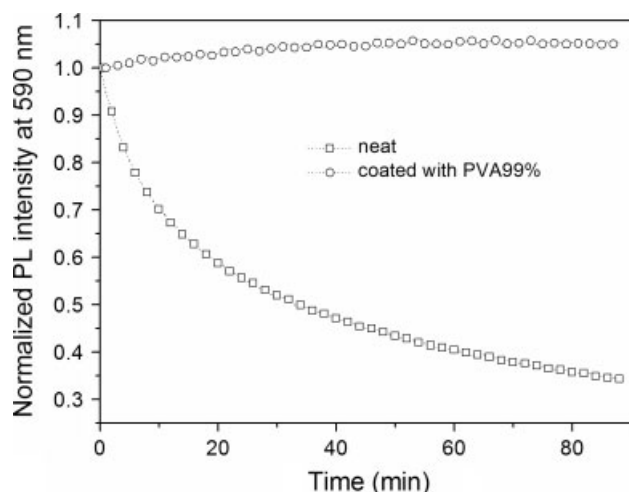
Figure 6. Normalized emission decay at 590 nm of OC$_1$OC$_6$-PPV films cast on glass neat and coated with PVA.

CONCLUSIONS

Among the coatings tested for the protection of PPV derivative films against photodegradation, the best results were obtained with 99% hydrolysed PVA. The total degradation time for the films coated with PVA increased by *ca* 700 times compared to the neat PPV derivative film with similar thickness, probably due to the lower permeability of oxygen through the PVA layer. The results show the great potential of this coating in minimizing and controlling the effects of photodegradation in films of PPV derivatives, which can be useful in applications to sensors, as, for example, in sensors for oxygen exposure. The effects PVA coatings on the electrical properties of PPV derivatives are now under study.

ACKNOWLEDGEMENTS

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